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17/74 19/10 19/12 19/24 21/14  
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(54) A recording sheet

(57) A recording sheet for use with pigment-based inks has a usable surface that includes a combination of a water soluble cationic substance and water soluble binder substance. The recording sheet may in particular be a natural tracing paper or an uncoated cellulose-based paper. The pigment-based ink is preferably applied to the recording sheet by an ink jet plotter or printer. The cationic substance may be a polyvalent metal salt, e.g. magnesium sulphate, or a polymeric amine, e.g. poly-quaternary amine. The binder may be polyvinylpyrrolidone, polyvinyl alcohol, carboxymethyl cellulose, starch or gelatine.

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RECORDING SHEET FOR USE WITH PIGMENT-BASED INKS

The present invention relates to a recording sheet for use with printers and plotters employing pigment-based inks. In particular, but not exclusively, the invention relates to tracing papers for use with ink jet plotters and printers. The invention is also applicable to other recording media, such as opaque papers, coated papers and plastics films, that are designed for use with printers and plotters employing pigment-based inks. For example, the invention also relates to opaque papers used for graphic arts applications. Preferably, the recording media are also compatible with other types of ink and other printers.

15 Natural tracing paper (as opposed to "prepared" tracing paper, also known as "vellum") is manufactured from wood-based cellulose fibre pulp, which is mechanically treated, for example by crushing and chopping, to remove any air/fibre interfaces. This renders the paper material translucent. The finished tracing paper is relatively dense and impervious compared with normal opaque papers.

Tracing papers have been used for many years for the preparation of engineering master drawings to be reproduced by the diazo process. Although manual drafting has largely been superseded by the use of CAD systems, tracing papers are still used for printing the master drawings. Various types of plotter are used for printing the drawings, including pen plotters and electrostatic printers, but one of the most favoured types of plotter at present is the ink jet plotter.

Some ink jet print heads available at present use dye-based inks. These are satisfactory for most general purpose applications such as printing text and some graphic material, but lack the density and permanence of the pigment-based inks that have traditionally been used in the preparation of engineering master drawings. The lower density of the ink means that drawings printed using dye-

bas d inks ar not as well suited to the diazo process as those produced using pigment based inks.

More recently, an ink-jet print head that uses pigment-based inks has become available. This print head produces denser images than the previous dye-based ink print heads and the resulting drawings are better adapted to the diazo copying process. The images are also less liable to fading than images produced using dye-based inks.

10

The development of the new ink jet print head has required the parallel development of new types of pigment-based ink. As the speed and definition of the print head has increased, the formulations of these new inks have been revised to provide the necessary performance.

A pigment-based ink for use with an ink jet print head typically comprises a dispersion of pigment particles, such as carbon black, suspended within an aqueous vehicle. Other ingredients, such as surfactants and stabilizers, are usually included to help maintain the dispersion, to prevent blocking of the ink jet nozzles and to promote vaporisation of the ink in the print head. However, unlike traditional pigment-based inks such as Indian ink, a binder such as shellac is not generally included as this can lead to blocking of the ink jet nozzles.

The applicants have identified a problem with existing tracing papers when used with ink jet print heads employing pigment-based inks. This is that when relatively large blocks or areas (i.e. areas larger than a few mm<sup>2</sup>) of high density are printed, the print can become rather uneven. For example, the print density may be reduced towards the edges of the area and stripes or patches of varying density may be produced. This phenomenon is sometimes referred to as "cascading". The variations in density are particularly notic able by transmitted light and they can, therefore, be

transferred to copies made by the diazo process. The effect is not generally particularly noticeable by reflected light or in as far as of text or fine details.

5 The applicants have observed that the above-mentioned problem occurs when the ink droplets fall onto the paper in such a concentration that they coalesce to form a pool of liquid ink on the surface of the paper. The applicants have discovered that when this happens, the pigment  
10 particles migrate towards one another within the pool of liquid, thereby forming areas of increased density and leaving areas of reduced density.

A similar problem has been observed with colour print heads  
15 that use pigment-based black ink and dye-based coloured inks. Where an area of pigment-based ink touches an area of dye-based ink, the border between the two inks becomes scalloped with the coloured dye-based inks intruding into the black area. The applicants have discovered that this  
20 effect is caused by migration of the pigment particles away from the area of dye-based ink.

It is an object of the invention to provide a recording sheet that mitigates at least some of the above-mentioned  
25 problems.

According to a first aspect of the invention there is provided a recording sheet for use with pigment-based inks, wherein at least a usable surface of the recording sheet  
30 includes a combination of a water soluble cationic substance and water soluble binder substance.

In experiments involving the application of various surface treatments to the recording sheet, the applicants found  
35 that by treating the surface of the sheet with a water soluble cationic substance, the suspension of pigment particles could be destabilized as the ink droplets hit the

surface, giving good print quality. However, abrasion resistance of the print was unsatisfactory. The printed documents did not, therefore, have the longevity required of them. The applicants discovered that this was because  
5 the pigment particles tended to sit on the surface of the paper, where they were exposed to abrasive forces, rather than being drawn into the structure of the paper.

The applicants have further found, however, that if the  
10 surface of the recording sheet is also treated with a water soluble or water-swellaable binder, the resistance of the ink to abrasion is greatly increased. Therefore, by treating the recording sheet with a binder substance in combination with a cationic substance, migration can be  
15 largely prevented and the print quality and permanence of the printed sheet thereby improved.

The cationic substance may be a soluble polyvalent metal salt. Suitable metal salts include the salts of metals  
20 from Groups II and III or the Transition Metals of the Periodic Table. Preferably, the metal salt is a salt of a cation selected from the group consisting of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Zr^{4+}$  and  $Zn^{2+}$ . Examples of suitable metal salts include magnesium sulphate, calcium chloride, ammonium sulphate,  
25 zinc acetate, ammonium zirconium carbonate and magnesium acetate.

Alternatively, the cationic substance may be a cationic polymer, and is preferably a low molecular weight, high  
30 cationic charge density, water soluble organic polymer. For example, the polymer may be a polymeric amine (such as a quaternary amine or easily protonated tertiary amine). A suitable cationic substance is a solution in water of a poly-quaternary amine.

35

The binder substance may be selected from a group consisting of polyvinylpyrrolidone (PVP), polyvinyl alcohol

(PVOH), carboxymethylcellulose (CMC) (especially low molecular weight carboxymethylcellulose), starches (for example oxidised potato starch and potato starch ethers) and gelatine (compounded animal protein in water). Various  
5 types of polyvinyl alcohol (PVOH) may be used, including those having a low hydrolysis level and a high molecular weight, a low hydrolysis level and a low molecular weight, a high hydrolysis level and a high molecular weight, or a high hydrolysis level and a low molecular weight. The  
10 binder substance may have a molecular weight in the range 790,000 to 1,350,000 and a viscosity defined by a K-value of at least 30, and preferably at least 60, and advantageously approximately 90.

15 In a particularly preferred embodiment of the invention, the cationic substance is magnesium sulphate and the binder is PVP. The amount of magnesium sulphate applied to the surface of the recording sheet is preferably in the range 0.5-3.0gsm ( $\text{gm}^{-2}$ ), and more preferably 1.0-2.0gsm, and  
20 advantageously approximately 1.25-1.75gsm. The amount of PVP applied to the surface of the recording sheet is preferably in the range 0.15-0.75gsm, and more preferably 0.4-0.7gsm, and is advantageously approximately 0.5gsm.

25 The invention is particularly applicable to natural tracing paper. The invention may also be applied to opaque paper and card, synthetic paper, coated paper or card and plastics film.

30 According to a second aspect of the invention, there is provided a natural tracing paper, wherein at least a usable surface of the paper includes a combination of a water soluble cationic substance and water soluble binder substance.

35

According to a third aspect of the invention, there is provided an uncoated, cellulos -based paper, wherein at

least a usable surface of the paper includes a combination of a water soluble cationic substance and water soluble binder substance.

5 According to a fourth aspect of the invention, there is provided a method of manufacturing a recording sheet for use with an ink jet plotter or printer, wherein at least a usable surface of the recording sheet is treated with a combination of a water soluble cationic substance and water  
10 soluble binder substance.

The recording sheet is advantageously treated by applying a solution of the combination of substances to the usable surface of the sheet. Preferably, the solution is applied  
15 by drawing the semi-manufactured recording sheet through a bath of the solution. Alternatively, the solution may be applied to the recording sheet by spraying or coating, either during or after completion of the manufacturing process.

20

According to a fifth aspect of the invention, there is provided a method of printing in which a pigment-based ink is applied to a recording sheet, wherein at least a usable surface of the recording sheet includes a combination of a  
25 water soluble cationic substance and water soluble binder substance.

Preferably, the pigment-based ink is applied to the recording sheet by an ink jet plotter or printer.

30

Various embodiments of the invention will now be described by way of the following examples, in which all parts and percentages are by weight unless otherwise stated.

### 35 Examples

The effect of applying various substances to natural



tracing paper was tested by applying the substances as aqueous solutions to a base paper comprising a 90gsm waterl af natural tracing paper. Th effectiveness of the substances in reducing migration was assessed visually and  
5 the substances were ranked according to the categories excellent, fair, mediocre and poor (in descending order). The effectiveness of the substances in binding the printed image to the paper was tested by visually assessing the results of an abrasion test and the substances ranked  
10 according to the same categories. The results of the tests are summarised in the following table (Table 1).

The tests revealed that whilst treating the surface of the paper with a cationic substance alone helps to reduce  
15 migration, this leads to poor resistance to abrasion. In order to provide good abrasion resistance as well as reduced migration, a binder must be applied in addition to the cationic substance. It was found that an aqueous solution comprising a blend of magnesium sulphate and high  
20 viscosity PVP produced excellent results, both for reducing migration and providing good resistance to abrasion.

Table 1: Test results.

	Solution content	Class	Blend	Applied weight	Binding rating	Migration rating
5	Aluminium sulphate	Cation	no	8.0 gsm 1.1 gsm	poor poor	excellent fair
	Calcium chloride	Cation	no	1.1 gsm 8.9 gsm	poor poor	good excellent
	Magnesium sulphate	Cation	no	1.0 gsm 8.5 gsm	poor poor	good excellent
	Polymeric quaternary amine	Cation	no	1.0 gsm 11.1gsm	poor poor	fair fair
	Oxidised potato starch	Binder	no	5.9 gsm 1.2 gsm	fair poor	poor poor
10	Potato starch ethers	Binder	no	1.5 gsm 3.6 gsm	poor fair	poor poor
	Polyvinyl alcohol (High hydrolysis, Low mol wt)	Binder	no	1.0 gsm 2.3 gsm	fair fair	poor poor
	Polyvinyl alcohol (Low hydrolysis, Low mol wt)	Binder	no	1.0 gsm 2.3 gsm	excellent excellent	poor poor
15	Polyvinyl alcohol (High hydrolysis, High mol wt)	Binder	no	0.4 gsm 0.8 gsm	excellent excellent	poor poor
	Polyvinyl alcohol (Low hydrolysis, High mol wt)	Binder	no	0.4 gsm 1.3 gsm	mediocre mediocre	poor poor
	Low viscosity PVP	Binder	no	0.1 gsm 0.5 gsm	excellent excellent	poor poor
20	Low viscosity CMC	Binder	no	0.4 gsm 0.1 gsm	fair fair	poor poor
	High viscosity PVP	Binder	yes	0.2 gsm	excellent	excellent
	Magnesium sulphate	Cation		1.0 gsm	excellent	excellent
	High viscosity PVP Magnesium sulphate	Binder Cation	yes	0.1 gsm 0.9 gsm	excellent excellent	excellent excellent

## CLAIMS

1. A recording sheet for use with pigment-based inks, wherein at least a usable surface of the recording sheet  
5 includes a combination of a water soluble cationic substance and water soluble binder substance.
2. A recording sheet according to claim 1, wherein the cationic substance is a soluble polyvalent metal salt.  
10
3. A recording sheet according to claim 2, wherein the cationic substance is a salt of a metal from Groups II and III or the Transition Metals of the Periodic Table.
- 15 4. A recording sheet according to claim 3, wherein the cationic substance is a salt of a cation selected from the group consisting of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Zr^{4+}$  and  $Zn^{2+}$ .
5. A recording sheet according to claim 4, wherein the  
20 cationic substance is magnesium sulphate.
6. A recording sheet according to claim 5, wherein the amount of magnesium sulphate applied to the surface of the recording sheet is in the range 0.5-3.0gsm, and preferably  
25 1.0-2.0gsm, and advantageously approximately 1.25-1.75gsm.
7. A recording sheet according to claim 1, wherein the cationic substance is a cationic polymer.
- 30 8. A recording sheet according to claim 7, wherein the cationic substance is a poly-quaternary amine.
9. A recording sheet according to any one of the preceding claims, wherein the binder substance is selected  
35 from a group consisting of polyvinylpyrrolidone, polyvinyl alcohol, carboxymethyl cellulose, starches and gelatine.

10. A recording sheet according to claim 9, wherein the binder substance has a molecular weight in the range 790,000 to 1,350,000.
- 5 11. A recording sheet according to claim 9 or claim 10, wherein the binder substance is polyvinylpyrrolidone having a viscosity defined by a K-value of at least 30, and preferably at least 60 and advantageously approximately 90.
- 10 12. A recording sheet according to claim 11, wherein the amount of PVP applied to the surface of the recording sheet is in the range 0.15-0.75gsm, and preferably 0.4-0.7gsm, and is advantageously approximately 0.5gsm.
- 15 13. A recording sheet according to any one of the preceding claims, in which the substances are applied to the surface of the recording sheet as an aqueous solution.
14. A recording sheet according to any one of the  
20 preceding claims, in which the recording sheet is a natural tracing paper.
15. A natural tracing paper, wherein at least a usable surface of the paper includes a combination of a water  
25 soluble cationic substance and water soluble binder substance.
16. An uncoated, cellulose-based paper, wherein at least a usable surface of the paper includes a combination of a  
30 water soluble cationic substance and water soluble binder substance.
17. A method of manufacturing a recording sheet for use with an ink jet plott r or printer, wherein at least a  
35 usable surface of the recording sheet is treat d with a combination of a water soluble cationic substance and water soluble binder substance.

18. A method according to claim 17, wherein the recording sheet is treated by applying an aqueous solution of the combination of substances to the usable surface of the sheet.

5

19. A method according to claim 18, wherein the solution is applied by drawing the semi-manufactured recording sheet through a bath of the solution.

10 20. A method of printing, in which a pigment-based ink is applied to a recording sheet, wherein at least a usable surface of the recording sheet includes a combination of a water soluble cationic substance and water soluble binder substance.

15

21. A method according to claim 20, wherein the pigment-based ink is applied to the recording sheet by an ink jet plotter or printer.



Application No: GB 9511363.5  
Claims searched: 1-21

Examiner: Alexander Littlejohn  
Date of search: 18 January 1996

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK CI (Ed.O): B2E (EM); D1R (RBX, RDL, REX, REZ, RFA)  
Int CI (Ed.6): B41M 1/36, 5/00; D21H 17/44, 17/45, 17/72, 17/74, 19/10, 19/12, 19/24, 21/14  
Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB2147003A (Ricoh) see whole document, e.g. page 1 lines 33-65 and page 3 lines 16-24	1-21
X	GB1351391 (Wiggins Teape) see whole document, e.g. page 1 lines 34-42 and page 2 lines 23-48	1,7-10, 13-21
X	EP0514633A1 (Schoeller) see whole document, e.g. claim 1	1,7-10, 13-21
X	EP0487350A1 (Xerox) see whole document, e.g. page 4 lines 38-47 and 54,55	1,7-10, 13-21
X	EP0423829A1 (Oji) see whole document, e.g. page 4 lines 47-50 and 54,55	1,7-10, 13-21
X	EP0164196A1 (Mead) see whole document, e.g. pages 9,10, page 14 lines 12-29 and Example 6 on page 25	1-21
X	WPI Abstract Accession No. 89-321746/44 & JP 1241487 A (Mitsubishi) (26-09-89) see abstract	1,7-10, 13-21
X	WPI Abstract Accession No. 88-351208/49 & JP 63264391 A (Sanyo) (01-11-88) see abstract	1,7-10, 13-21

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